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Deuterium Tracer Studies on the Course of Addition to Norbornene. IX

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A comparison of the course of addition of DBr to norbornene under polar and free radical reaction conditions has been carried out. The circumstances of these experiments have presumably involved no extraneous or endemic directive effects. The results of polar addition can be reconciled (only) with a single path consistent with a cationic intermediate, in contrast to reports of a multiplicity of pathways for addition to substituted norbornenes. The failure to find significant amounts of *trans* addition product with DBr where other unsymmetrical addition reagents (*i.e.*, Br₂, ArSCl, etc.) are known to follow this reaction route points clearly to the existence of directive substituent influences and the intermediacy of onium ion (or stable π) complexes in the latter reagents. The free radical course, as has been previously suspected, was found to be strikingly different. The major product is the result of *cis-exo* addition *unaccompanied* by any rearrangement that could be traced *via* the deuterium label. About one-fifth of the total product arises from the unusual process of attack by bromine radicals from the *endo* side of the double bond. The possible occurrence of a bromine bridged radical in the course of forming this (*endo*) material as well as the other minor product, *exo-trans*, has been given some consideration, but the dominant pathway of the radical addition appears to be subject to steric control of product formation from the carbon radical intermediate.

The additions to norbornene and substituted norbornenes have recently been studied and summarized.¹ In general, the results of the polar additions considered were interpreted on the assumption of π -complexes and bridged cation intermediates. Since then, however, the occurrence of complexes² and nonclassical carbonium ions³ in polar addition reactions has been brought into question and the evidence upon which the earlier conclusions were based was re-examined. This has been made possible in some cases by the availability of newer analytical techniques. A particular case in point is the study by Cristol and co-workers^{4,5} of the course of addition of polar reagents to trimethylenenorbornene.

In contrast to the ionic mechanisms of addition in which bridged ions, or their equivalent equilibrium of ionic structures, have been invoked to explain the kinetic and stereochemical results, it has been repeatedly suggested that analogous evidence for bridging in free radical addition mechanisms is not to be found in the bicyclic system.^{6,7} However, the very recent report by Skell, Tuleen, and Readio⁸ of stereochemical evidence for radicals involving bromine bridging urges re-study of these earlier conclusions.

In most of the reactions studied, whether ionic or free radical, a commonly suspected² influence has been the ability of either an already existing substituent, or a group, having entered in the attack stage of the reaction, directing the course (*cis*, *trans*, or rearranged) of the second stage. For instance, in the reaction of X⁺Y⁻ with norbornene (the question may be asked) what is the influence of X in the intermediate carbonium ion or radical controlling the position and ease of bond formation with Y in the product-forming step? When the entering group X is hydrogen, no directive influence should be operating, but the problem of analyzing the stereo-

chemical course of the addition reaction arises. If deuterium is substituted for the hydrogen, the products formed *via* the various possible routes would no longer be identical and could be distinguished by an appropriate degradation scheme. Again, the possible intrusion of deuterium isotope effects (in particular) on the course and facility of the addition reactions has to be confronted, but, in general, such effects are of secondary nature.

Our selection of DBr as the preferred reagent for investigation was dictated by several considerations. A study of the competitive elimination of HBr and DBr with strong base from appropriate norbornyl bromide preparation (as well as analogous norbornyl tosylate) was carried out for the purpose of providing a basis for interpreting the results of the suggested degradative scheme. This study is reported elsewhere.⁹ In addition, the availability of some very fine background in the literature of deuterium isotope effects in general elimination reactions^{10,11} and in related systems¹² presented a basis for estimating the proper magnitudes of deuterium isotope effect corrections of the analytical data. Finally, the (DBr) reagent of choice, being capable of undergoing both free radical and ionic additions to norbornene, afforded us thereby a direct comparison of these two mechanisms of addition to bicyclic olefins which has not been previously accessible.

Results

The polar addition of DBr to norbornene was carried out with a 47.5% DBr solution in D₂O, using suitable protection against the incursion of a photocatalyzed reaction. The mixture was stirred vigorously at 60° for 3 hr. and afforded a better than 80% yield of pure *exo*-norbornyl bromide. No contamination of the product with the *endo* epimer could be detected by vapor phase chromatographic techniques.

The free radical addition of DBr to norbornene was performed in hexane solution using a quartz flask reactor and irradiating with an ultraviolet source to

(1) L. Kaplan, H. Kwart, and P. von R. Schleyer, *J. Am. Chem. Soc.*, **82**, 2341 (1960), and references cited therein.

(2) M. J. S. Dewar and R. C. Fahey, *ibid.*, **85**, 2245, 2248 (1963).

(3) See discussion pertinent to ref. 16.

(4) S. J. Cristol, W. K. Leifert, D. W. Johnson, and J. B. Jurale, *J. Am. Chem. Soc.*, **84**, 3918 (1962).

(5) S. J. Cristol, L. K. Gaston, and D. W. Johnston, *Tetrahedron Letters*, **4**, 185 (1963).

(6) S. J. Cristol, G. D. Brindell, and J. A. Reeder, *J. Am. Chem. Soc.*, **80**, 635 (1958), and many references cited therein.

(7) S. J. Cristol and G. D. Brindell, *ibid.*, **76**, 5699 (1954).

(8) P. S. Skell, D. L. Tuleen, and P. D. Readio, *ibid.*, **85**, 2349 (1963).

(9) H. Kwart, T. Takeshita, and J. L. Nycy, *ibid.*, **86**, 2606 (1964).

(10) V. J. Shiner, *ibid.*, **76**, 1603 (1954).

(11) W. H. Saunders, Jr., and D. H. Edison, *ibid.*, **82**, 138 (1960).

(12) N. A. LeBel, P. D. Beirne, E. R. Karger, J. C. Powers, and P. M. Subramanian, *ibid.*, **85**, 3199 (1963).

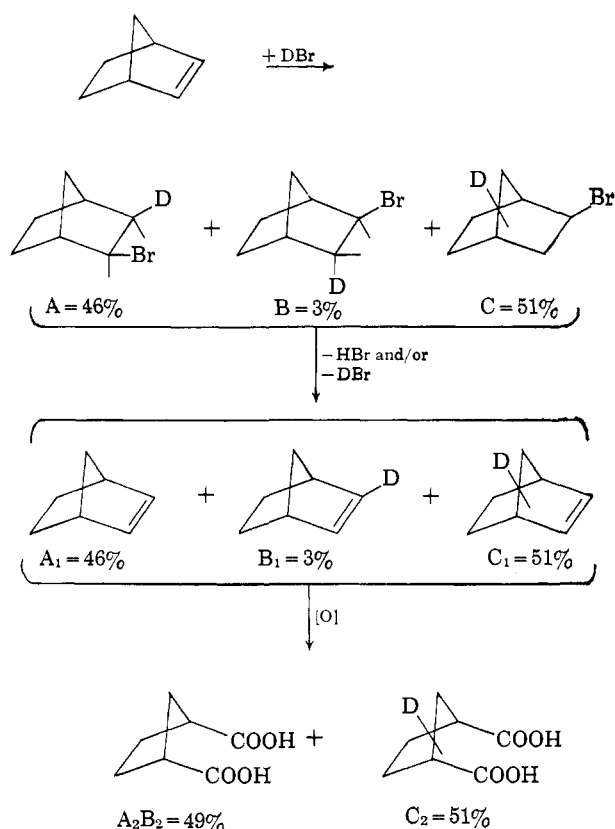


Fig. 1.—Flow diagram of polar addition of DBr.

nearly 80% completion. The product obtained here, in distinction to the polar addition, consisted of a mixture of the epimers in the approximate ratio of 20% *endo*- to 80% of the *exo*-norbornyl bromide, as determined both by infrared spectrophotometry and vapor phase chromatography. As noted in our equilibration studies,⁹ the occurrence of any thermodynamic control of product formation is to be correlated with formation of some *endo* epimer. We therefore deduce that our product is the result of control by kinetic factors alone.

The products of both procedures (respectively) were subjected to a degradative routine, involving dehydrohalogenation with strong base as the first step with isolation of the norbornene in good yield, followed by oxidation to the *cis*-1,3-cyclopentanedicarboxylic acid. The product at each juncture was analyzed for its deuterium content to determine how the results could be correlated with the mode of addition. The results are summarized in Table I.

TABLE I

	Polar addition ^a	Free radical addition ^b
Norbornyl bromide	100	100
Norbornene	54	38.6
<i>cis</i> -1,3-Cyclopentanedicarboxylic acid	51 ^c	0 ^d

^a The base used for elimination was 3-methyl-3-pentoxide in 3-methyl-3-pentanol at 120°. ^b The base used for elimination was 3-methyl-3-pentoxide in *p*-cymene at 130°. ^c In other runs of this reaction a maximum of 58% of the deuterium was found in the acid. ^d The only circumstances under which any deuterium was retained here were those occurring in solvents in which some concomitant polar addition was suspected.

Discussion

The Polar Addition of DBr to Norbornene.—It has earlier been proposed that when X^+Y^- is added to the norbornene¹³⁻¹⁵ skeleton in the absence of any directive

substituent influence, the exclusive product to be observed is the norbornyl derivative with Y in the *exo* configuration. Our experimental results (above), applying the newer analytical techniques which were not available to the earlier workers, confirm this conclusion (only) for the polar addition. Any *endo* product would have been readily detected, as will be shown later. When X is hydrogen attack by Y at the C₃- or C₄-positions in cation I cannot be equivalent. Our use of



Cation I; X = H or D

Cation II, X = polar group; *viz.* Br, SAR, etc.

DBr, however, does permit a distinction (that is not possible with HBr) in that, by means of the degradative procedures mentioned above, the alternative modes of attack (by Y^- or its equivalent) are correlatable with the deuterium distribution. The over-all loss of 49% deuterium (Table I) in the sequence leading to the diacid end product (A_2B_2) is in good agreement with expectation on the basis of either a nonclassical structure or the equilibrium of classical structures depicted for cation I. In the nonclassical ion the C₃- and C₄-positions are exactly equivalent since a plane of symmetry exists as defined by C_{1,6,5} and the midpoint of the C_{3,4}-bond. In the classical ion equilibrium, a steric argument called the "windshield wiper effect" has been advanced¹⁶ to anticipate this result. Of course, 50% attack should be expected at each of the C₃- and C₄-atoms only if we ignore any possible directive effect of a deuterium at C₂.

In the light of repeated demonstrations^{12,17,18,19} of favored *cis* elimination of HY from norbornane derivatives by means of strong base, the reactions outlined in Fig. 1 are very readily interpreted. It will be seen that three structures can result from the addition of DBr to norbornene, the *cis*-*exo* product (A), *trans* (B), and a rearranged product (C) in which the deuterium is bonded anywhere except on the same ethylene bridge as the bromine atom. It is very evident from the degradative sequence outlined in Fig. 1 and the data in Table I that C must comprise 51% of the total addition product and A + B the remaining 49%, since C is the only one of the three products which would retain deuterium in the dibasic acid terminus. Of the deuterium content (49%) that is not accounted for by the structures C, C₁, and C₂, fully 94% is lost during the dehydrohalogenation step ($A + B \rightarrow A_1 + B_1$) and the residue, or about 6%, is retained in B₁.

Several alternative explanations of these data may be considered: (1) a 6% proportion of D^+ *endo* attack completed by *trans* addition to form structure B and

(13) J. D. Roberts, E. R. Trumbull, Jr., W. Bennett, and R. Armstrong, *J. Am. Chem. Soc.*, **72**, 3116 (1950).

(14) L. Schermerling, *ibid.*, **68**, 195 (1946).

(15) J. D. Roberts, L. Urbanek, and R. Armstrong, *ibid.*, **71**, 3049 (1949).

(16) H. C. Brown, Abstracts, 139th National Meeting of the American Chemical Society, St. Louis, Mo., March 21, 1961, p. 2-O; "Non-Classical Intermediates," Organic Reaction Mechanisms Conference, Brookhaven, N. Y., Sept. 5, 1962.

(17) S. J. Cristol and E. F. Hoegger, *J. Am. Chem. Soc.*, **79**, 3438 (1957).

(18) S. J. Cristol and H. L. Hanse, *ibid.*, **74**, 2193 (1952).

(19) C. H. DePuy, R. D. Thurn, G. F. Morris, D. K. Wedegaertner, and J. A. Beckman, Abstracts, 142nd National Meeting of the American Chemical Society, Los Angeles, Calif., April, 1963, p. 9M.

all-*cis* elimination; (2) no *endo* addition of D[⊕], (B = 0), but 6% of *trans* elimination occurring in A with removal of the *endo* proton; or (3) a combination of circumstances 1 and 2. The very considerable body of evidence demonstrating a preference for *exo* attack^{2,5} in the norbornyl system does not *per se* rule out explanation 1 since we have found that in the free radical addition (see later section) about 20% of the reaction product may be formed through initial attack from the *endo* bonding direction. This reservation, however, is weakened by the knowledge that in the polar reaction the analogous attacking reagents are considerably enlarged by solvation and tend to be more discriminating with regard to the steric environment of the locus of attack. Cristol and co-workers⁵ have expressed the view that initial *endo* attack in polar addition is quite unlikely on the bicyclo[2.2.1]heptane ring. To be taken into consideration here also are the results of LeBel and co-workers¹² who have reported that in the elimination reaction under similar conditions of base strength and temperature, $k_{cis}/k_{trans} \cong 15$ and $k_H/k_D \cong 3.4$. Furthermore, they have found that an *exo* is abstracted about three times more readily than a corresponding *endo* proton, which implies that the k_H/k_D preference is just about cancelled out by the k_{exo}/k_{endo} preference. It seems reasonable, then, that the observed 6% formation of B₁ (of the total of A₁ + B₁) is in good accord with the occurrence of a minor amount of *trans* elimination accompanying a predominant course of *cis* elimination, as suggested by explanation 2.

Admittedly, it cannot be claimed that an exclusive path has been compellingly demonstrated for the formation of component B which comprises (only) less than 3% of the polar addition product. It seems very clear, however, that the great majority of the product consists of just two components, A and C, developing in nearly equal amounts, whose formation path may be conceived without resort to equivocation. Our data, in fact, are consonant with several interesting conclusions which may be summarized as follows.

Since the polar addition of DBr is unbiased with respect to forming rearranged and nonrearranged products, this result stands in marked contrast to the analogous case of *endo*-trimethylenenorbornane, which has been reported by Cristol and co-workers⁵ to undergo polar addition of the elements of DOCH₃ with production preponderantly (>80%) of rearranged materials. Evidently, the remote trimethylene substitution has exerted some directive influence in the product-forming step, an influence which does not exist in the unsubstituted norbornene. Furthermore, unlike the substituted case presented by Cristol, *et al.*,⁵ our data do not compel the requirement of two alternative paths or intermediates in the polar addition reaction. A single structure such as cation I may be reconciled with the common intermediate which, uninfluenced by remote substituent effects, leads with equal probability to both rearranged and unrearranged products. This identification of cation I is further enhanced by the observation of an exclusive preference for *cis* addition in formation of the unrearranged product. *Trans* product formation *via* a protonated π -complex^{3,20,21} is here excluded.

It must be emphasized that both the occurrence of *trans* and assorted nortricyclic products^{2,21} and the proportions of rearranged and unrearranged product found in a given case are the consequences of the operation of factors which are not endemic to the polar mechanism of addition to the bicyclic double bond. Thus, as has been suggested earlier,² the formation of *trans* addition product from bicyclic olefins can be anticipated where the addition reagent is capable of forming a relatively stable π -complex or onium ion in the attack phase of the reaction as, for example, is characteristic of such reagents as Br₂ or ArSCl. The product composition will be deviated, also, where substituent effects are evident—either resulting from the influence of a remote substituent already resident on the ring, or one introduced *via* attack of the electron deficient moiety of X⁺Y^{-δ} with formation of a cationic intermediate like II, possessing (now) a substituent capable of directing the subsequent product-forming phase of the reaction.

Free Radical Addition of DBr to Norbornene.—The intervention of a nonclassical, bridged free radical structure in free radical additions to acyclic and monocyclic olefins has never been substantiated.⁶ Convincing demonstrations of the classical character of additions of *p*-thiocresol to norbornene^{6,22} and other bicyclic compounds^{6,23} have been presented. This conclusion has usually been inferred from the failure to find any rearrangement product in the reaction mixture.

While the nonstereospecific nature of radical addition mechanisms has been widely reported,^{24,25} a number of exceptions involving stereospecific addition of hydrogen bromide may be cited.²⁶ The latter may be regarded as special cases of steric control where the product-forming step is completed at the side of the intermediate radical which is least hindered by the bulky bromine atom attached at the adjacent carbon.

The product obtained by working up the photo- and peroxide-catalyzed reaction of dry HBr and norbornene (in the cold) was found to be similar in infrared spectrum to that of pure *exo*-norbornyl bromide except for six extra bands of moderate intensity. By admixing various proportions of the pure *exo* isomer with this product, all of these six bands decreased in intensity while the other bands remained substantially constant. Finally, some pure *endo*-bromide was prepared by the Diels-Alder reaction of vinyl bromide and cyclopentadiene²⁷ followed by hydrogenation over platinum. The *exo*-bromide was separated by exhaustive solvolysis making use of the large difference in rates of the *exo* and *endo* epimers in this reaction, as previously noted.²⁸

(21) See ref. 2 as well as H. Kwart and R. K. Miller, *J. Am. Chem. Soc.*, **78**, 5678 (1956).

(22) S. J. Cristol and R. P. Arganbright, *ibid.*, **79**, 6039 (1957).

(23) J. A. Berson and W. M. Jones, *ibid.*, **78**, 6045 (1956).

(24) See C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, for a general review of the early literature on this subject.

(25) (a) F. G. Bordwell and W. A. Hewett, *J. Am. Chem. Soc.*, **79**, 3493 (1957); (b) H. L. Goering, D. I. Relyea, and D. W. Larsen, *ibid.*, **78**, 348 (1956).

(26) (a) H. L. Goering, P. I. Abell, and B. F. Aycock, *ibid.*, **74**, 3588 (1952); (b) H. L. Goering and L. L. Sims, *ibid.*, **77**, 3465 (1955); (c) H. L. Goering and D. W. Larsen, *ibid.*, **79**, 2653 (1957); **81**, 5937 (1959); (d) P. S. Skell and R. G. Allen, *ibid.*, **80**, 5997 (1958); **81**, 5383 (1959); **82**, 1511 (1960).

(27) K. Alder and H. F. Rickert, *Ann.*, **543**, 1 (1939).

(28) (a) J. D. Roberts, W. Bennett, and R. Armstrong, *J. Am. Chem. Soc.*, **72**, 3329 (1950); **76**, 4623 (1954); (b) S. Winstein, H. M. Walborsky, and K. Schreiber, *ibid.*, **72**, 5795 (1950).

(20) G. S. Hammond and T. D. Nevitt, *J. Am. Chem. Soc.*, **76**, 4121 (1954); C. H. Collins and G. S. Hammond, *J. Org. Chem.*, **25**, 911 (1960).

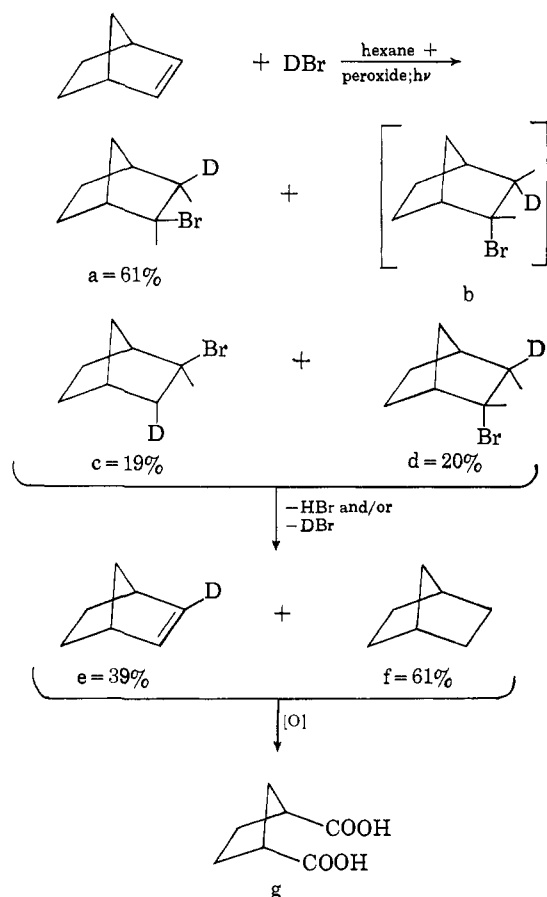


Fig. 2—Flow diagram of free radical addition of DBr.

The solvolysis was repeated until the infrared and v.p.c. showed no further change. Using this standard in the v.p.c. determination helped to establish that the free radical addition of DBr to norbornene had given rise to both the *exo*- and *endo*-bromides, the latter comprising about 20% of the total. Estimation from the infrared spectral data was also in agreement with this figure.

No attempt was made to separate the product into the isomeric components and the total product was degraded by the same sequence of reactions discussed previously for the polar addition. The results are summarized in Table I. Several other additions were attempted using CCl_4 as solvent. In one case some product of reaction of the norbornene with this solvent was obtained. In two other cases, evidently, some polar addition had also occurred since a small amount of rearranged product was found, as indicated by the presence in such cases of a small amount of deuterium retention in the terminal diacid g, Fig. 2.

The appearance of about 20% of *endo*-bromide was somewhat surprising. This, however, is not the only instance that might be construed as *endo* attack in a free radical addition to the bicyclic olefin. LeBel and co-workers¹² have also observed an analogous occurrence in the free radical addition of HBr to 2-chloronorbornene, in which the resident 2-chloro could conceivably be exerting a directive influence. No such influence can be invoked to explain *endo* attack (as we here have observed) in norbornene.

The total (possible) composition of the radical addition reaction product may be examined by means of the flow diagram in Fig. 2. Initially, let us assume that b

can be reasonably excluded as a component of the product mixture. (We will return to this point and attempt to justify the assumption later in the discussion.)

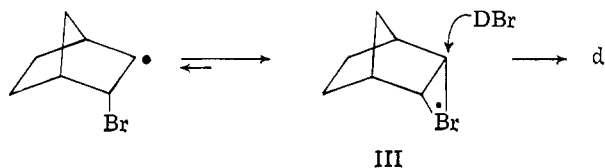
The complete absence of a rearrangement course of radical addition is here made obvious by the isolation of only the isomeric *endo*- and *exo*-norbornyl bromides. Furthermore the dibasic acid end product of the degradation series, g, possesses no trace of deuterium (beyond natural abundance). When we scrutinize the product structures in Fig. 2 individually, we note: (1) In a the magnitude of $k_H/k_D \cong 3.4$ is effectively cancelled out by the weight of $k_{exo}/k_{endo} \cong 3$ and (what we have come to consider in this system as) normal *cis* elimination^{12,17-19} takes place with complete loss of deuterium to give f. (2) In structure c the preference for *exo* elimination and the primary deuterium isotope effect work in the same direction and both re-enforce the preference for *cis* elimination to give structure e possessing the remainder of the original deuterium label. (3) The structure d, as noted earlier, corresponds to about 20% of *endo* attack by bromine atoms. Here, also, the preference for *cis* elimination and re-enforcement by the primary deuterium isotope effect would be expected to outweigh completely the noted favor for *exo* proton abstraction and consequently prevent significant loss of deuterium when d experiences the elimination reaction.

This reasoning process leads to the deduction that structure a, the only isomer capable of deuterium loss during elimination, must be present in the radical addition product to the same extent as f, namely 61%. Since c and d constitute the remainder capable of forming structure e on elimination, and since d has been estimated to be ca. 20% by v.p.c. and infrared analysis, the products c and d are *trans* addition products and together they comprise nearly 40% of the total addition product, the other 60% (as noted above) being directly correlated with *cis* addition.

To justify the assumption (made earlier) that b may be excluded as a possible component of the reaction mixture, we turn to consideration of the known factors controlling the steric course of radical addition reactions.^{25,26} The *exo-cis* addition product a is evidently (at least) the *predominant* precursor of the undeuterated olefin f, in keeping with the established *cis* course of elimination and the observed 4/1 excess of *exo*- over *endo*-bromo product formation. Steric control of the stereochemistry of radical addition reactions has previously been strongly indicated.²⁶ Since the *exo* aspect of the norbornyl ring is the sterically more accessible,² the predominant formation of the *exo-cis* addition product a is quite consistent with the inference of steric control of *both* the initial bromine radical attack step and the product-determining reaction of the resulting carbon free radical intermediate.

Any possibility for formation of an *endo-endo* product b is apparently in opposition to the manifest preference of both the bromine radical attack step and the product-forming step to occur from the *exo* direction. Furthermore, even in the event of *endo* attack by bromine, (a 1 to 4 probability compared to *exo*) only a maximum yield of ca. 4% of b could be expected on the basis of steric control of the product-forming step which (as seen from our data) has, again, only a 1 to 4 probability of being completed on the *endo* side. Aside from these steric

factors, other considerations would seem to vitiate an ensuing reaction to form *b* from the carbon radical resulting from initial *endo*-bromine atom attack and, thus, even further reduce the probability of producing *b* below this 4% upper limit. For example, we may suppose that some facility for *endo* attack could derive from stabilization afforded the resulting radical intermediate *via* bromine bridging (III).



However, Skell and his co-workers,⁸ who have discovered such bridging interaction by α -halogen, have also demonstrated that the subsequent product-forming step occurs exclusively with inversion and only *d* can be anticipated as the product of the reaction course. From all these considerations, in fact, *d* is the most satisfactory structural assignment which can be made for the *endo*-norbornyl bromide.

Finally, several additional inferences may be drawn from our results. First, in the formation of *ca.* 20% *endo*-norbornyl bromide a reaction course has been realized which is peculiar to the radical mechanism of addition and has no analog in the attack of solvated cations on the bicyclic double bond *via* the polar mechanism.⁵ Secondly, it seems obvious that the (60%) *cis* addition product *a* could *not* have arisen from any kind of nonclassical radical or bromine bridged radical intermediate,⁸ since the former would lead us to anticipate an accompanying quantity of rearranged product (not found), and the latter demands an over-all *trans* addition course. Furthermore, both *c* and *d*, the *ca.* 40% of the total product arising from *trans* addition, could conceivably have been formed through the intervention of a bromine bridged radical⁸ or some radical species akin to a π -complex. The close similarity in the proportions of *c* and *d* might then be regarded as suggestive evidence of the operation of such a bromine-bridged radical mechanism with little or no stereoselectivity; *i.e.*, the greater stability of the bromine-bridged radical intermediate is reflected in a lowering of the steric barrier to attack in the *endo* orientation, so that both *endo* and *exo* radicals are formed with comparable ease.

Experimental

Preparation of Deuteriobromic Acid.—Deuterium oxide of 99.5% enrichment was obtained from Stuart Oxygen Co. and was used in all of the experiments.

Deuterium oxide (22 g.) was added slowly to 110 g. of rapidly stirred phosphorus tribromide to generate the deuterium bromide which was dissolved in 110 ml. of cold deuterium oxide. A positive pressure of dry nitrogen was maintained in order to prevent the solution from sucking back. The constant boiling azeotrope of deuteriobromic acid (47.5% DBr) was then distilled and the fraction boiling at 124–126° was collected.

Polar Addition of Deuteriobromic Acid to Norbornene.—The 47.5% deuterium bromide solution (192.5 g.) was added to 54 g. of norbornene (0.57 mole) and warmed at 60° for 3 hr. The organic layer was separated and the aqueous layer extracted several times with ether. The combined ether and organic layers were washed with water until the washings were neutral. The ether solution was dried over anhydrous calcium sulfate, the ether stripped off at atmospheric pressure, and the residue vacuum distilled through a Vigreux column. The total yield of *exo*-

norbornyl bromide was 85.4 g. The center cut taken from this constant boiling material at 63.4° (10.5 mm.) was redistilled into glass ampoules and sealed off under vacuum in preparation for the deuterium analysis; literature value¹³ 84–87° at 31 mm. The v.p.c. showed only a single peak for all cuts and there seemed no need to be concerned about fractionation.

Free Radical Addition of Deuterium Bromide to Norbornene.

—The free radical addition of deuterium bromide to norbornene was carried out in a quartz flask equipped with a magnetic stirrer, reflux condenser, and gas inlet tube; the flask was irradiated with an ultraviolet light throughout the reaction. The deuterium bromide, generated as previously described and passed through anhydrous CaSO₄, was allowed to bubble through 50 g. of norbornene dissolved in either CCl₄ or hexane containing 0.5 g. of benzoyl peroxide. An excess of deuterium bromide was passed through the rapidly stirred solution. The addition took about 3.5 hr. and the solution was allowed to stir for another half-hour. The organic solution was then washed with water and dried over anhydrous sodium sulfate. The solvent was removed at atmospheric pressure and the residue vacuum distilled to give 70.6 g. of norbornyl bromide (76% yield). The material balance could be accounted for by the unreacted norbornene collected as a forecut in the distillation. The infrared spectrum of the pure material from a free radical HBr addition showed bands at 10.35, 11.6, 12.07, and 13.24 μ which were absent in a spectrum of pure *exo*-norbornyl bromide but present in a spectrum of *endo*-norbornyl bromide. Two bands were found at 11.4 and 11.94 μ which were absent in a spectrum of pure *endo*-norbornyl bromide but present in the spectrum of the *exo* isomer. Various other bands were of intermediate intensity between those found for the pure isomers and changed in intensity as the mixture of *endo* and *exo* isomers was changed. The gas chromatography results confirmed the presence of the two isomers and indicated 20% of the *endo* isomer was present, in rough agreement with the results estimated from the infrared spectra. The infrared spectrum of the deuterium compound was found to be quite different, as is usually the case in this system, but gas chromatography indicated that the proportion of isomers was about the same.

Oxidation of Norbornene.—The procedure of Birch and co-workers²⁹ was used in the oxidation of norbornene. The yields of *cis*-1,3-cyclopentanedicarboxylic acid were generally in the neighborhood of 90% or more. The best procedure for purification was found to be sublimation, after several recrystallizations from both nitromethane and water. After sublimation the pure compound melted at 120–121°.

Dehydrobromination of Deuterio-*exo*-norbornyl Bromide.—The potassium salt of 3-methylpentanol-3 was prepared by dissolving 8.0 g. of potassium in 140 g. of the alcohol. To the cooled solution 23.7 g. of deuterio-*exo*-norbornyl bromide was added and a tan precipitate began to form immediately. The solution was heated at reflux temperature for about 24 hr., after which it was poured into 200 cc. of water and extracted with ether. The ether extracts were dried over anhydrous potassium carbonate and distilled at atmospheric pressure through a Widmer column. The cut from 90 to 105° was collected and redistilled several times until the norbornene solidified in the receivers. The pure norbornene was then redistilled from sodium and the middle cut boiling at 95–96° was collected for the deuterium analysis. The maximum yield obtained by this technique was 80%. In some cases, as mentioned earlier, *p*-cymene was used in place of the alcoholic solvent. Further details of this procedure are reported elsewhere.⁹

Purification of *endo*-Dehydronorbornyl Bromide.—The general procedure followed was that of Roberts and co-workers.^{28a} The distilled product mixture from the Diels–Alder reaction of cyclopentadiene and vinyl bromide was put into 100 ml. of 80% alcohol containing 10 g. of NaOAc·3H₂O. The mixture was stirred rapidly at reflux temperature for 19.5 hr. Upon isolation of the product it was found that a large amount of ether impurity was present which could not be fractionated, so another attempt was made using acetone and water with lithium carbonate. The solution was refluxed for 40 hr. this time. The product was distilled twice through a Widmer type column to give two fractions, b.p. 68.2–69°, *n*_D²⁰ 1.5190 and 1.5192. These cuts were combined for infrared analysis and gas chromatography. The infrared spectrum indicated that a small amount of alcohol impu-

(29) S. F. Birch, W. J. Oldham, and E. A. Johnson, *J. Chem. Soc.*, 818 (1947).

rity was present (about 7% by v.p.c.). The v.p.c. also showed that no more than 1% of the *exo* isomer was still present.

Method of Deuterium Analysis. Combustion.—A standard type combustion train was assembled which was large enough to handle samples up to 125 mg. The main combustion tube was packed according to the directions outlined by Niederl³⁰ for combustion of compounds containing carbon, hydrogen, sulfur, and halogen. The water was collected in a modified U-tube immersed in a Dry Ice-acetone bath. After the combustion was completed the tubes were cut from the system with a torch so that the water was completely sealed from any atmospheric moisture.

Dilution of Samples.—If the deuterium content was estimated to be higher than three atom per cent, the sample was diluted with distilled, demineralized water. This was done by transferring the sample by means of micropipet to a pear shaped container of about 1 cc. volume. The dilution was done by weight on an analytical balance. After dilution, the sample was stoppered with a clean, dry rubber serum stopper and rotated for at least 20 hr. to ensure proper mixing.

Calibration Curve for Infrared.—The calibration standards were made up gravimetrically from deuterium oxide and water carefully distilled and demineralized; the maximum range represented was 0.0 → 3.3 atom % deuterium oxide. If more than 1 week lapsed between determinations, a new calibration curve was made; otherwise, at least one point was checked each day.

Determination of Deuterium Oxide Content.—The relative atom per cent of D₂O and H₂O contained in the water mixture after combustion was determined by use of infrared analysis as described by Trenner and co-workers.³¹ A single beam Beckman Model IR 2A was used with a specially thermostated Perkin-Elmer microcell, 127-xx18.³² The temperature was held constant within ±0.1°. The temperature control is necessary owing to the large temperature coefficient of the absorbance of the O-D

band at 3.98 μ. The spectrophotometrical measurement of the O-D band is made possible by the magnitude of the shift in wave length of the stretching frequency (2.8 to 3.98 μ). This shift accompanies the substitution of a deuterium atom for one of the hydrogen atoms of water.

The technique employed in the determination was essentially the same as that described by Trenner.³¹ The cell was filled by applying gentle suction by means of a standard hypodermic syringe. The cell was placed in the thermostated cell holder and allowed to come to temperature for about 10 min. Good (averaged) *I*-values were then obtained for the sample (*I_x*) and standard (*I₀*); these values were measured on the recorder paper with reference to the dark line. The relative absorbance is simply log *I₀*/*I_x*. From these values the per cent D₂O in the sample was determined, reference being made to the calibration curve previously described.

TABLE II

DATA OBTAINED FROM THE ANALYSIS FOR DEUTERIUM CONTENT

	Theoretical ^a atom % D	Corrected atom % D ^b	Found atom % D ^c	Deuterium lost, %
Polar addition				
Norbornyl bromide	9.09		8.24	
Norbornene	10.0	9.06	4.90	46
Cyclopentanedicarboxylic acid	10.0	9.06	4.60	49
Free radical addition				
Norbornyl bromide	9.09		6.28	
Norbornene	10.0	6.91	2.67	61.4
Cyclopentanedicarboxylic acid	10.0	6.91	0.00	100

^a Calculated on the basis that one atom of deuterium existed in place of one atom of hydrogen in each compound. ^b Since only 8.24 atom % deuterium (90.6% of the theoretical) had been introduced during the addition to form norbornyl bromide, the corresponding theoretical values for the degradation products required appropriate corrections. ^c Found experimentally by the infrared method described elsewhere in this Experimental section.

(30) B. Niederl and J. B. Niederl, "Micromethods of Quantitative Organic Analysis," John Wiley and Sons, Inc., New York, N. Y., 1942.

(31) (a) *Perkin-Elmer Instrumental News*, 4, No. 1 (1952); (b) N. R. Trenner, B. H. Arison, and R. W. Walker, *Appl. Spectry.*, 7, No. 4 (1953); (c) N. R. Trenner, B. H. Arison, and R. W. Walker, *Anal. Chem.*, 28, 530 (1956).

(32) "Instruction Manual, Perkin-Elmer Infrared Equipment," Vol. 2, The Perkin-Elmer Corp., Norwalk, Conn., 1952, pp. 5-6.

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Deuterium Tracer Studies on the Elimination Reactions of Norbornyl Tosylate and Bromide. XI

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The elimination reaction of *exo*-norbornyl tosylate with strong base in tertiary alcohol solvent proceeds with indications of considerable E1 character, yielding only about 18% *cis* elimination product. The same reaction in hydrocarbon solvent medium occurs with a "pure" E2 mechanism and results in about 65% *cis* elimination. Norbornyl bromide appears to undergo *cis* elimination nearly exclusively (98%) via a concerted E2 process even in the tertiary alcohol medium, when appropriate correction is made for a deuterium isotope effect. These results are discussed in the light of *cis* and *trans* elimination (E2) requirements recently formulated by DePuy and co-workers. The most attractive interpretation of the E1 elimination pattern, in consonance with recent studies in acyclic systems, appears to justify the assumption of an intimate ion pair intermediate.^{29,30}

Introduction

Our present knowledge of the elimination reaction recognizes a spectrum of possibilities lying between the extremes of mechanism. We approach at one end the carbanion (E1CB) mechanism which finds the β-proton bond completely ruptured in the transition state. On the other is located the fully formed carbonium ion (E1) mechanism. The most usual expressions of the E2 mechanism² calls for concerted action in which

abstraction of the β-proton and separation of the leaving group occur simultaneously. Recent studies, however, have disputed the generality of this picture and indicate that these two steps do not necessarily take place synchronously. Bunnett and co-workers³ have presented the case of "E2 leaning toward E1."

Investigations seeking to establish the existence of the E1CB mechanism can be grouped in two categories: (1) cases studied in which the *trans* coplanar stereochemical requirement of the E2 mechanism cannot be satisfied,⁴⁻⁹ and (2) cases studied in which the β-proton

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(2) The terms E1CB, E2, and E1 are defined by C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, Chapter 8.

(3) J. F. Bunnett, G. T. Davis, and H. Tanida, *J. Am. Chem. Soc.*, 84, 1606 (1962).